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Diffusion of Tritiated Water in Soils[1]

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ABSTRACT

The apparent diffusion coefficient of tritiated water (D_{THO}) was measured in four soil materials and two sizes of glass beads at about 40% water content by volume, and in agar gel. The apparent tritiated water diffusion coefficient may include diffusion in the liquid, vapor, and possibly adsorbed phases. For Pachappa loam, D_{THO} was determined in detail as a function of water content. The D_{THO} was nearly constant for volumetric water contents of 10 to 40%. As the water content decreased below 10%, the D_{THO} rapidly increased to a maximum at about 4% water content, then rapidly decreased as the water content was further reduced. The maximum value of D_{THO} is 3.5 times greater than D_{THO} at 40% water content.

SOME ASPECTS of problems concerning water movement in soil-water systems appear amenable to solution by use of isotopic tracers. Before such studies can be properly evaluated, the behavior of the isotopic tracer within the soil-water system in the absence of water movement caused by pressure or concentration gradients must be ascertained. This is especially true when water is labelled with one of its constituent isotopes such as H^2, H^3, and O^{18}. Such labelled water molecules diffuse in the liquid, vapor, and adsorbed phases and also exchange with water molecules adsorbed on clay surfaces.

When using any isotopic tracer, an important aspect that must be considered is whether the tracer behaves like the bulk material being traced. Kaufman and Orlob (6), in evaluating several ground-water tracers, had measured a smaller rate of water movement in the soils when using tritiated water (THO) than when using salt tracers. They ascribed this behavior to a replacement of the water already present in the soil or to an exchange with the clay mineral constituent. Earlier experiments (4, 9) have shown the exchange of deuterated water (DHO) can occur with externally and interlamellarly adsorbed water of clay minerals and also with the hydroxyl group of the clay mineral surfaces.

Wang and co-workers (12, 13) have performed numerous studies of "self-diffusion" of water molecules. They observed that water molecules labelled with H^2, H^3, or O^{18} behaved like water molecules and that the mechanism of rapid proton transfer, which would limit the use of H^2 or H^3 as a water tracer, does not appear as it does in the case of electrolytic conduction of hydrogen ions.

Kunze and Kirkham (8) studied the diffusion of deuterated water in soil-water and glass bead-water systems and considered the measured diffusion coefficient as the "self-diffusion" coefficient of water. They found the diffusion coefficient for DHO to be more than twice as large in the glass bead-water than in the soil-water system and attributed this difference to adsorptive forces in the soil-water system.

The use of water labelled with H^2, H^3, or O^{18} in soil-water investigations is limited because special analytical instruments and accessory equipment required for such studies are not readily available in many soil research laboratories. A method for studying soil-water movement using DHO in which the deuterium is determined spectrometrically has been described by Kunze and Kirkham (8). Nakayama (10) has discussed the equipment for, and some applications of, the use of THO in soil- and plant-water investigations.

This paper describes a method for the measurement of diffusion of tritiated water and also presents data of D_{THO} in four soil-water systems, two glass bead-water systems, and agar gel. Since we are concerned with the behavior of an isotopic tracer, we avoid using the term "self-diffusion" and refer only to the diffusion of tritiated water. Furthermore, we use the term "apparent diffusion coefficient" to imply that diffusion of tritiated water may take place in liquid, vapor, and adsorbed phases, either separately or in any combination.

THEORY

The measurement of the apparent diffusion coefficient of tritiated water involved the chemical analysis of the tracer throughout the soil column after an instantaneous plane source of the tracer was placed at one end of the column. The equation which describes the concentration of tracer at any distance and time under these conditions is

$$\partial c/\partial t = D\ \partial^2 c/\partial x^2, \qquad [1]$$

where c is the concentration of tracer, t the time, D the apparent diffusion coefficient, and x the distance. The symbols c, D, and x apply to the porous medium as a whole, and not solely to the fluids within the pores.

Equation [1] is strictly valid for one-phase diffusion in an isotropic medium. However, on a macroscale a soil-water system approximates an isotropic medium, and diffusion in the liquid, vapor, and adsorbed phases may be represented by an apparent diffusion coefficient.

If the medium is sufficiently long and the duration of the experiment is sufficiently short so that the concentration does not change at the end opposite $x = 0$, then the column can be assumed to be semi-infinite in length and a solution of equation [1] applicable to this problem is

$$c = Q(\pi Dt)^{-1/2} \exp(-x^2/4Dt) \qquad [2]$$

where Q is the quantity of diffusing component deposited at the plane $x = 0$ (1).

In the derivation of equation [2] it is assumed that diffusion takes place in a homogeneous medium of uniform cross section. If the soil columns meet these conditions, the activity of the diffusing tracer in the column is directly proportional to the concentration and equation [2] can be written in terms of tracer activity instead of concentration. Replacing c in equation [2] with A, the activity of the tracer per unit bulk volume, and Q with A_T, the total activity deposited at the plane $x = 0$, and integrating over x yields

$$A_X/A_T = \text{erf}\ x/(4Dt)^{1/2}, \qquad [3]$$

where A_x is the activity in the column over the distance $x = 0$ to $x = x$. The notation erf is the error function whose value is tabulated in mathematical handbooks such as that published by the National Bureau of Standards (11).

The diffusion coefficient is calculated by measuring A_x/A_T for a particular x and obtaining the associated value of the error function argument $[x/(4Dt)^{1/2}]$ from the tables. Since x and t are known, D is easily calculated. In practice we measure A_x/A_T at several x's, calculate D for these several x's and average the values obtained.

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MATERIALS AND METHODS

The apparent diffusion coefficient of tritiated water was determined in agar gel ("Difco" Bacto-agar),[3] glass beads (Minnesota Mining and Manufacturing Company),[3] and four soil materials. Three concentrations of the gel, 0.50, 0.75, and 1.00% were prepared from steam-sterilized agar solutions. The 70°C. agar solution was poured into columns with special care to prevent entrapment of air bubbles and was allowed to solidify slowly to room temperature. The sizes of glass beads were 28μ and 203μ. The four soil materials were Adelanto loam, Colo clay loam, Fort Collins loam, and Pachappa loam. Particle size analyses for the four soil materials are presented in table 1. Air-dry soil materials, previously passed through a 2-mm. sieve, and the glass beads were packed into columns with a mechanized column packer (5). The columns were wetted horizontally using a fritted glass bead plate such that the pressure potential of water at the center of the column was −2mb. The equilibrium water contents under these conditions were Adelanto 38.5%, Colo 44.0%, Fort Collins 36.8%, Pachappa 36.5%, 28μ glass beads 35.9%, and 203μ glass beads 34.9% by volume. In addition, different water contents were used for Pachappa loam. Water contents between 9 and 36.5% were obtained by extracting the water from the saturated soil column in a pressure cooker apparatus. Water contents $< 9\%$ or $>$ air-dry were obtained by equilibrating the previously saturated soil material in the pressure membrane apparatus. These materials were hand-packed into the columns. One sample of 28μ glass beads was brought to a water content of 17.8%.

Columns were constructed from 3.2-cm.-inside-diameter lucite cylinders cut into 1-cm. sections. The 1-cm. sections were taped together to make columns of the desired length. Lengths ranging from 10 to 44 cm. were used.

To initiate a diffusion measurement, one end of the partially sealed column containing a sample was fitted with a filter-paper disk. A 0.01-ml. volume of 100-μc. per ml. THO solution, which was prepared from 100-mc. per ml. stock solution, was spread on the filter paper and the column then sealed and stored at 25 ± 2°C. The column was protected from light during storage by wrapping it with aluminum foil. After contact periods of 1 to 20 days, depending upon the sample, the column was sectioned into 1-cm. or longer sections. Water was extracted from the sample by a vacuum technique in which the water vapor was condensed into a detachable cold-finger trap at approximately −72°C. using a bath of dry ice and alcohol. A 30- to 45-minute vacuum dehydration period was found to be equivalent to an oven-drying treatment at 105°C.

[3]Trade names and company names are included for the benefit of the reader and do not infer any endorsement or preferential treatment of the products on the part of the U. S. Department of Agriculture.

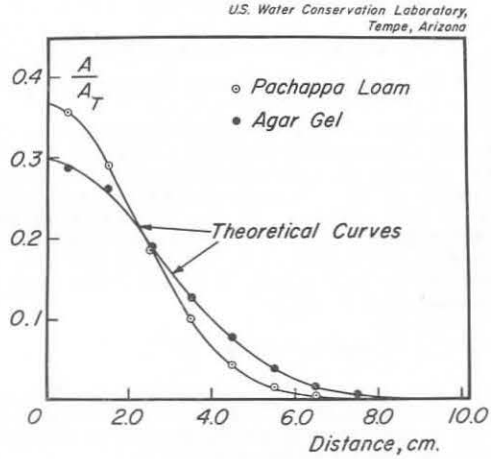

Figure 1—Comparison of experimental and theoretical tritiated water distribution in agar gel and Pachappa loam columns, where the experimentally determined D's are 2.11 × 10^{-5} and 1.37 × 10^{-5} cm.^{2} per sec., respectively, and exposure period is 48 hours.

The THO activity in the extracted water was determined using a modified Kinard liquid scintillation solution (2, 7) and the Baird-Atomic Model 745A liquid scintillation equipment.

RESULTS AND DISCUSSION

Examples of the relation between A/A_T and x for a sample of 1% agar gel and of Pachappa soil at 11% water content are presented in figure 1. The points are experimental values and the lines are theoretical curves calculated with equation [2] using the average D_{THO} obtained from equation [3]. The experimental points fall on the theoretical curves, a necessary, but not necessarily sufficient, result for the verification of the theory and its underlying assumptions.

The diffusion coefficients for THO in agar gel and glass beads are listed in table 2. Agar gel was used to check the technique and to get an estimate of D_{THO} in pure water. By measuring D_{THO} in agar gel at several concentrations (0.5, 0.75, 1.0%), plotting the measured D_{THO} as a function of concentration, and extrapolating to zero agar concentration, an estimate of D_{THO} in pure water was obtained. This value was 2.40 × 10^{-5} cm.^{2} per sec., which is in good agreement with the value of 2.44 × 10^{-5} cm.^{2} per sec. measured in pure water by Wang et al. (13).

The D_{THO} in glass beads (table 2) was approximately 30% lower than D_{THO} in pure water. This decrease is probably due to the increase in path length or tortuosity created by the presence of solid particles. The apparent diffusion coefficients were similar for the three glass bead-water systems. However, a slightly higher value of D_{THO} was measured for the 28μ beads at 17.8% water content than at the higher water content of 35.9%. Kunze and Kirkham (8) give a value of 1.36 × 10^{-5} cm.^{2} per sec. for D_{DHO} in a 28μ glass bead-water system, about 20% lower than our 1.69 × 10^{-5} cm.^{2} per sec.

The diffusion coefficients of THO in four soil materials at one water content for each soil are presented in table 3. The highest value of D_{THO} was for Pachappa, the soil with the lowest clay content, and the lowest D_{THO} was for Colo, the soil with the highest clay content. Adelanto and Fort Collins exhibited intermediate values of D_{THO} and clay contents. The D_{THO} in two samples of Colo clay loam at 33.7 and 44.0% water contents at bulk densities of 1.17 and 1.23 g. per cm.^{3}, respectively, was 0.87 ×

Table 1—Particle size analysis of soil materials used in THO diffusion studies.

Sample	Sand (> 50μ)	Coarse silt (20-50μ)	Fine silt (2-20μ)	Clay (< 2μ)	Textural class
	%	%	%	%	
Adelanto	31.6	24.2	21.8	22.4	Loam
Colo	21.9	13.6	31.9	32.6	Clay loam
Fort Collins	40.6	20.0	16.0	23.4	Loam
Pachappa	41.6	36.6	13.3	8.5	Loam

Table 2—Diffusion coefficient of THO in agar gels and glass beads.

Material	Composition	Water content, % by volume	Total porosity, %	Diffusion coefficient, cm.^{2}/sec. × 10^5
Agar gel	0.0*	-	-	2.40
Agar gel	0.50%	-	-	2.27
Agar gel	0.75%	-	-	2.21
Agar gel	1.00%	-	-	2.15
Glass beads	28μ	35.9	38.1	1.56
Glass beads	28μ	17.8	38.1	1.69
Glass beads	203μ	34.9	37.6	1.68

* Extrapolated value, see text.

Table 3—Diffusion coefficient of THO in four soil materials.

Soil	Water content, % by volume	Total porosity, %	Diffusion coefficient, $cm.^2/sec. \times 10^5$
Adelanto loam	38.5	44.3	1.01
Colo clay loam	44.0	56.0	0.87
Fort Collins loam	36.8	47.6	1.08
Pachappa loam	36.5	45.9	1.14

10^{-5} cm.^{2} per sec. Kunze and Kirkham (8) reported D_{DHO} for Colo clay loam at 37.5% water content and bulk density of 1.25 g. per cm.^{2} to be 0.61×10^{-5} cm.^{2} per sec., about 30% lower than our D_{THO}.[4] The differences observed cannot be explained on the basis of the difference in the physical condition of the materials nor on the types of tracers used. The D_{THO} and D_{DHO} in pure water are similar. Wang (12) and Wang et al. (13) reported values of 2.44×10^{-5} cm.^{2} per sec. and 2.34×10^{-5} cm.^{2} per sec. for D_{THO} and D_{DHO}, respectively. Note that the D_{THO} was greater than D_{DHO}, while one would predict on the basis of molecular weight of DHO and THO that D_{DHO} should be greater than D_{THO}. There is no reasonable explanation for this difference, although experimental error may account for it.

The diffusion coefficients of tritiated water in Pachappa loam at different water contents are shown in figure 2. In the water content region between 10 and 40% by volume the D_{THO} is almost constant, ranging from 1.37 to 1.10×10^{-5} cm.^{2} per sec. These values are approximately one-half that for the diffusion of D_{THO} in bulk water. The D_{THO} of 4.16×10^{-5} cm.^{2} per sec. at about 4% water content, the maximum value observed, was about 6,000 times smaller than the diffusion coefficient of water vapor in air, which is 0.257 cm.^{2} per sec. at 25°C. (3). The value 4.16×10^{-5} may not be the true maximum.

Note the sharp increase in D_{THO} when the water content decreased from 10 to 4%, and the equally sharp decrease in D_{THO} when the water content decreased to values $< 4\%$. The sharp rise in D_{THO} which starts at 10% and continues to 4% was probably the result of an increase in the number of continuous pores available for vapor diffusion; the sharp decrease in D_{THO} below 4% is probably the result of the adsorptive force field of the soil particles acting upon the diffusing tracer molecules. These forces are present throughout the entire moisture range, but manifest themselves to a greater degree at the low water contents where the tracer molecules diffusing in the vapor phase have a greater probability of colliding and exchanging with the adsorbed molecules. Surface area calculation indicates that for this soil, two molecular layers of water are present on the particle surface when the water content is about 4%.

If diffusion were solely in the liquid phase, one might expect D_{THO} to decrease with a decrease in the water content. This would be because the path length through the liquid would increase as water content decreases. However, as the water content decreases air enters the larger pores. The ensuing vapor phase provides an additional pathway for the diffusion of THO. Diffusion can proceed in series and in parallel within the two phases. Since the diffusion coefficient of water vapor in air is 10^4 greater than in pure water, one might then expect a rapid increase in diffusion as pores become air-filled. As stated earlier, neither situation was the case for Pachappa loam between 10 and 40% water content. Apparently, within this water content range, vapor diffusion increased with decreasing water content in the same proportion as liquid diffusion decreased. At this time we can only speculate on the mechanisms involved.

[4]Our sample of Colo clay loam was furnished by Dr. Kunze. Our glass beads and those used by Kunze and Kirkham (8) were obtained from the same manufacturer.

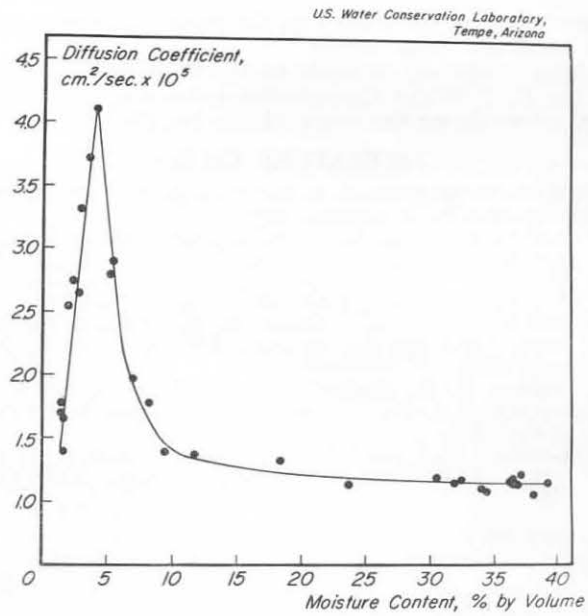

Figure 2—The apparent diffusion coefficient of tritiated water in Pachappa loam at different water contents.

Had the diffusion coefficient for THO been measured only at say 1.5, 10, 20, 30, and 40% water contents, one might have erroneously concluded that D_{THO} was essentially constant over the entire water content range. Detailed measurements must be made in order to delineate the peak. The occurrence of this type of D_{THO}-water content relationship for Pachappa loam does not necessarily imply that the same type of relationship will exist for other soils. This also means that if THO is to be used as a tracer for water in a particular soil-water system the diffusive behavior of THO must be determined in that system in order to properly evaluate the results.

SUMMARY AND CONCLUSIONS

The apparent diffusion coefficient of tritiated water (D_{THO}) was measured in four soil materials and two sizes of glass beads at about 40% water content by volume, and in agar gel. The term "apparent diffusion coefficient" is used to imply that diffusion may occur in liquid, vapor, and possibly adsorbed phases, and in any combination of the three. One soil material (Colo clay loam) and one size of glass beads (28μ) were comparble to those used by Kunze and Kirkham (8) in their diffusion studies with deuterated water (DHO). Water contents and bulk densities were similar in the two studies. Our measured D_{THO}'s exceeded Kunze and Kirkham's D_{DHO}'s by 20 to 30% in both systems. The difference could not be explained on the basis of the molecular weights of the tracers used.

For Pachappa loam, D_{THO} was determined in detail as a function of water content. The D_{THO} was nearly constant, ranging from 1.37 to 1.10×10^{-5} cm.^{2} per sec., at water contents between 10 and 40% by volume. As the water content decreased below 10%, the D_{THO} sharply increased to a maximum of 4.16×10^{-5} cm.^{2} per sec. at about 4% water content by volume, then sharply decreased as the water content was further reduced. The D_{THO} at 4% water content, the maximum value measured, is 3.5 times $> D_{THO}$ at 40% water content. Surface area calculation indicated that for this soil about two molecular

layers of water are present on the particle surfaces where the maximum D_{THO} occurs.

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